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Layered Double Hydroxides Intercalated by Polyoxometalate Anions with Keggin (α-$H_2W_{12}O_{40}^{6-}$), Dawson (α-$P_2W_{18}O_{62}^{6-}$), and Finke ($Co_4(H_2O)_2(PW_9O_{34})_2^{10-}$) Structures

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The pillaring of Mg_3Al layered double hydroxides (LDHs) by the title polyoxometalates (POMs) was accomplished by ion exchange reaction of the LDH−hydroxide and −adipate precursors with the POM anion at ambient or refluxing temperatures. The structural, thermal and textural properties of the LDH−POM intercalates were elucidated based on XRD, FTIR, TEM, EDS, and N_2 adsorption−desorption studies. A gallery height of ~10 Å was observed for the LDH intercalated by the symmetrical Keggin POM, whereas two different gallery heights were found for the cylindrical Dawson (14.5 and 12.8 Å) and Finke (13.3 and 12.6 Å) anions, depending on the preparation temperature. The differences in POM orientations were rationalized in terms of different electrostatic and hydrogen-bonding interactions between the POM pillars and the LDH layers. Upon thermal treatment at ≥100 °C, the intercalated Dawson and Finke POM ions exhibited only one gallery orientation, regardless of synthesis conditions. The crystalline microporous structures were retained upon heating each LDH−POM intercalate in N_2 to 200 °C. Pillaring in all cases was accompanied by the formation of a poorly ordered Mg^{2+}/Al^{3+} salt impurity that formed on the external surfaces of the LDH crystals.

Introduction

There has been considerable interest in the design and applications of microporous pillared solids with "supergallery" structures[1−3] wherein the interlayer thickness or gallery height is substantially larger than that of the host layers.[2] This structural characteristic results in a two-dimensional, microporous intercalate in which most of the unit cell volume is contained in the chemically accessible gallery region rather than in the dense host layers. Among the various classes of ionic lamellar solids, layered double hydroxides (LDHs) are uniquely suited for pillaring by polyoxometalate (POM) anions, because they are the only known family of layered materials with permanent positive charge on the layers. Owing to the diversity of approaches to the design of these nanoscale materials,[4−11] a broad spectrum of physicochemical properties are possible. Most importantly, pillared microporous derivatives are accessible, by mediating the charge density of the host layers (lateral pore size control) and the size and charge of the pillaring POMs (longitudinal and lateral pore size control).

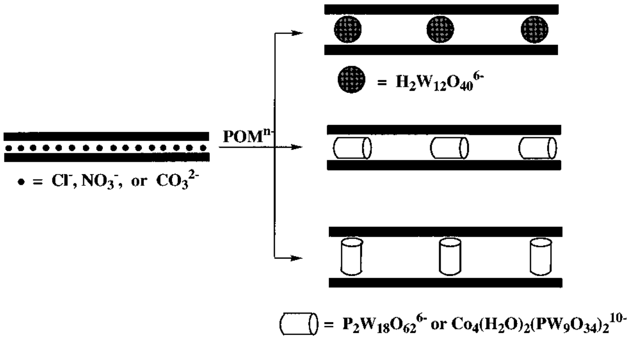

Figure 1. Schematic representation of the formation of LDH derivatives pillared by Keggin POM^{n-} ions with nearly spherical symmetry and by Dawson and Finke POM^{n-} ions with cylindrical symmetry.

Approaches to the preparation of pillared LDH−POM intercalates have been limited to date to the size of α-$H_2W_{12}O_{40}^{6-}$ Keggin structures,[4−11] which have a diameter (~10 Å) approximately two times as large as the LDH layer thickness (~4.8 Å). LDH derivatives pillared with larger POMs than Keggin ions are potentially more interesting for achieving increased access to the gallery space.

In the present work, we have undertaken a systematic approach to the synthesis of crystalline LDH intercalates interlayered by Dawson (α-$P_2W_{18}O_{62}^{6-}$) and Finke ($Co_4(H_2O)_2(PW_9O_{34})_2^{10-}$) structures with molecular diameters much larger than 4.8 Å, as well as the Keggin ion (α-$H_2W_{12}O_{40}^{6-}$) structure. As illustrated in Figure 1, each class of the POM can impart a different gallery pore structures upon pillaring reaction, resulting in new members of the class of LDH−POM derivatives. α-$H_2W_{12}O_{40}^{6-}$ with the T_d symmetry of the α-Keggin ion structure has a nearly spherical shape, which will limit the possible gallery heights upon intercalation in LDH galleries. On the other hand, the other two POMs with lower molecular symmetries can provide gallery micropores of different sizes, depending on their interlayer orientations. For example, the parallel and perpendicular gallery orientations of α-$P_2W_{18}O_{62}^{6-}$, with the D_{3h} symmetry of the Dawson structure, and of $Co_4(H_2O)_2(PW_9O_{34})_2^{10-}$, with the C_{2h} symmetry of the

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(1) Mitchell, I. V., Ed. *Pillared Layered Structures*; Elsevier: London, 1990.
(2) Pinnavaia, T. J. In *Expanded Clays and Other Microporous Solids*; Van Nostrand Reinhold: New York, 1992; p 1 and references therein.
(3) Clearfield, A.; Kuchenmeister, M. In *Supramolecular Architecture*; ACS Symposium Series 499; American Chemical Society: Washington, DC, 1992; p 128 and references therein.
(4) Kwon, T.; Tsigdinos, G. A.; Pinnavaia, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 3653.
(5) Drezdzon, M. A. *Inorg. Chem.* **1988**, *27*, 4628.
(6) Kwon, T.; Pinnavaia, T. J. *Chem. Mater.* **1989**, *1*, 381.
(7) Chibwe, K.; Jones, W. *Chem. Mater.* **1989**, *1*, 489.
(8) Dimotakis, E. D.; Pinnavaia, T. J. *Inorg. Chem.* **1990**, *29*, 2393.
(9) Wang, J.; Tian, Y.; Wang, R.-C.; Clearfield, A. *Chem. Mater.* **1992**, *4*, 1276.
(10) Narita, E.; Kaviratna, P. D.; Pinnavaia, T. J. *J. Chem. Soc., Chem. Commun.* **1993**, 60.
(11) (a) Ulibari, M. A.; Labajos, F. M.; Rives, V.; Trujillano, R.; Kagunya, W.; Jones, W. *Inorg. Chem.* **1994**, *33*, 2592. (b) Lopez, T.; Bosch, P.; Rames, E.; Gomez, R.; Novaro, O.; Acosta, D.; Figueras, F. *Langmuir* **1996**, *12*, 189.

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Finke structure, can result in 2.1 and 5.0 Å differences, respectively, in the pore size along the c direction of a layered LDH−POM intercalate. Differences in pillaring method, reaction temperature and time, and the use of a preswelling agent were considered in the present work as factors governing the intercalation of POM. The structural, thermal and textural properties of the pillared products were examined based on XRD, FTIR, TEM, EDS, and N_2 adsorption−desorption studies. The interlayer orientation of the gallery POMs was determined and rationalized in terms of electrostatic and hydrogen-bonding interactions between the gallery POMs and the LDH layers. Also, the nature of an impurity co-product formed in the intercalation reactions, which has been a subject of differing interpretations[9,10,12] was clearly demonstrated in the present work.

Experimental Section

Materials. Reagent grade chemicals were used as received. $Na_2WO_4 \cdot 2H_2O$ was a gift from GTE Sylvania Co. Adipic acid was purchased from Fisher. H_2WO_4, $Na_2HPO_4 \cdot H_2O$, and other reagents were purchased from Aldrich. Deionized water was used for the preparation of all aqueous solutions. The pH of reaction mixtures was monitored by a Fisher Model 750 selective ion analyzer. The ammonium salt of α-$H_2W_{12}O_{40}^{6-}$ and the potassium salts of α-$P_2W_{18}O_{62}^{6-}$ and $Co_4(H_2O)_2(PW_9O_{34})_2^{10-}$ were prepared by literature methods.[13−15]

Mg_3Al−LDH−Carbonate. An Mg_3Al−LDH−carbonate was prepared by a coprecipitation method at constant pH.[16] A 250-mL quantity of 1.0 M mixed-metal nitrate solution of Mg^{2+} and Al^{3+} (Mg^{2+}/Al^{3+} = 3.0) was added with vigorous stirring into 500 mL of water preadjusted with NaOH to pH 10.0 at 40 °C. The reaction pH was kept at 10.0 (±0.1) by the coaddition of a mixed solution of 1 M Na_2CO_3 and 2 M NaOH ($CO_3^{2-}/Al^{3+} = 1.5$). Upon the completed addition of the mixed-base solution the reaction pH was controlled by the addition of a 2 M NaOH solution. The resultant white suspension was further stirred for 3 h at 40 °C, and then the temperature was increased to 70 °C for 40 h. The white product was then filtered, washed with deionized water and dried in air at room temperature. ICP elemental analysis and thermogravimetric analysis (TGA) gave the composition $[Mg_{3.11}Al(OH)_{8.22}](CO_3)_{0.5} \cdot 9.8H_2O$.

Mg_3Al−LDH−Hydroxide (Meixnerite). An aqueous suspension of synthetic meixnerite (1.0 wt %) was prepared by the thermal decomposition of the corresponding Mg_3Al−LDH−carbonate and the subsequent reconstitution of the resulting mixed metal oxide solid solution into an LDH−hydroxide.[17] Mg_3Al−LDH−carbonate (1.0 g) was calcined in a quartz tube furnace for 5 h at 500 °C under a N_2 flow to form a solid oxide. The oxide then was transferred to a sealed flask containing 100 mL of degassed H_2O to form the LDH−hydroxide after a reaction time of 5 days. ICP Mg and Al analyses were indicative of the composition $[Mg_{3.08}Al(OH)_{8.16}](OH)_{1.0} \cdot xH_2O$.

Magnesium Hydroxide. Into 100 mL of vigorously stirred water preadjusted at pH 10.0 with 2 M NaOH was added slowly a 1.0 M Mg^{2+} nitrate solution (100 mL) at 40 °C. The reaction pH was kept at 10.0 (±0.1) by the addition of 2 M NaOH throughout the delivery of the nitrate solution and the subsequent 4 h reaction period at 40 °C. The white precipitate was allowed to age for 40 h at 70 °C. After cooling to room temperature, the product was filtered, washed with water, and dried in air at room temperature.

Pillaring of Mg_3Al−LDHs by POMs. Pillaring reactions were carried out under N_2 to avoid contact with atmospheric CO_2 during the reaction.. Deionized and decarbonated water was used to prepare all aqueous solutions. POM solutions (0.01−0.02 M) in 3-fold excess of the LDH anion exchange capacity (AEC) were used for the pillaring reactions.

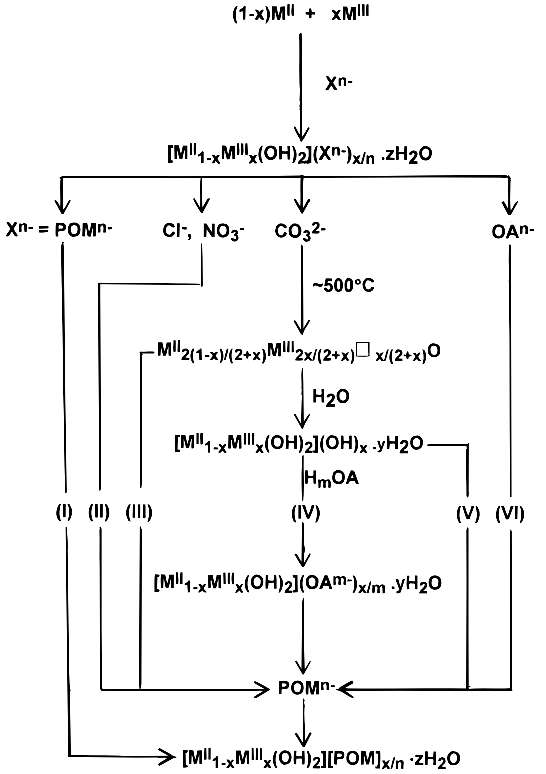

Figure 2. Summary of the synthetic methods used to prepare LDH intercalates pillared by POM^{n-} ions: (I) direct coprecipitation; (II) simple anion exchange; (III) calcined metal oxide; (IV and VI) organic precursor methods; (V) synthetic meixnerite method. Method IV uses synthetic meixnerite to prepared LDH−organic precursor, but the organic precursor in method VI is prepared by a co-precipitation during the synthesis of the LDH.

Figure 2 summarizes six different synthesis methods that have been reported in the literature[4−10] for the preparation of LDH−POM intercalates. In the present work, three of these pillaring methods, namely III, IV, and V, were examined to compare the crystallinity of products pillared by α-$H_2W_{12}O_{40}^{6-}$ Keggin ions.

Method III. A mixed metal oxide, freshly formed by calcining a Mg_3Al−LDH−carbonate at 500 °C under N_2 for 5 h, was added all at once to the POM solution at room temperature, as described by Chibwe and Jones.[7] The reaction mixture was then stirred for 30 h at room temperature under N_2. Upon being centrifuged and washed, the product was dried in air at room temperature.

Method IV. An aqueous meixnerite suspension was added to an adipic acid solution in 2-fold excess of the AEC, in order to form the corresponding Mg_3Al−LDH−adipate. After being allowed to stir for 1 h at 50 °C, the suspension was allowed to settle and then decanted, leaving a slurry of the LDH−adipate precursor. A 100-mL portion of degassed boiling water was added to the fresh LDH−adipate slurry, and then the hot suspension was added slowly to the POM solution at 100 °C under N_2. The reaction mixture was allowed to stir for an additional 0.5 h at reflux temperature, and the product was washed with water and dried in air.

Method V. An aqueous suspension of synthetic meixnerite was added dropwise to a POM solution under N_2 at room temperature, while the reaction pH was maintained at 4.5 by the co-addition of 0.01 M HNO_3. After being allowed to stir for an additional 0.5 h, the product was washed with water and dried in air. In an alternative procedure an aqueous meixnerite suspension was added dropwise to the POM solution at room temperature under N_2. After the completed delivery of the meixnerite, the reaction mixture was stirred for an additional period (0.5 or 5 h) at the same temperature without adjusting the pH. The solid product was then washed with water and dried in air. To

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(12) Weber, R. S.; Gallezot, P.; Lefebvre, F.; Suib, S. L. *Microporous Mater.* **1993**, *1*, 223.
(13) Mooney, R. W.; Chiola, V.; Hoffman, C. W. W.; Vanderpool, C. D. *J. Electrochem. Soc.* **1962**, *109*, 1179.
(14) Finke, R. G.; Droege, M. W.; Domaille, P. J. *Inorg. Chem.* **1987**, *26*, 3886.
(15) Evans, H. T.; Tourné, C. M.; Tourné, G. F.; Weakley, T. J. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2699.
(16) Yun, S. K.; Pinnavaia, T. J. *Chem. Mater.* **1995**, *7*, 348.
(17) (a) Sato, T.; Kato, K.; Endo, T.; Shimada, M. *React. Solids* **1986**, *2*, 253. (b) Sato, T.; Fujita, H.; Endo, T.; Shimada, M. *React. Solids* **1988**, *5*, 219.

examine the impact of reaction temperature on the product crystallinity, another set of reactions was carried at an elevated reaction temperature where the aqueous meixnerite suspension was added to the POM solution at 70 °C under N_2. The reaction mixture was then allowed to stir for 5 h before being washed and dried in air.

For α-$P_2W_{18}O_{62}^{6-}$ and $Co_4(H_2O)_2(PW_9O_{34})_2^{10-}$ as the pillaring anions, two reactions were carried out, one according to method IV using the LDH−adipate as the precursor at a reaction temperature of 100 °C and the other according to method V using a meixnerite precursor and ambient pH conditions at room temperature.

Physical Measurements. X-ray diffraction patterns were obtained with a Rigaku X-ray diffractometer equipped with DMAXB software and a curved graphite monochromator attachment for Cu Kα radiation. XRD patterns were recorded at room temperature for oriented film specimens (about 70 mg) supported on glass slides. X-ray diffraction patterns of samples preheated at 100 and 200 °C for 1 h under N_2 flow in a quartz furnace were obtained at room temperature.

Fourier transformed infrared (FTIR) spectra of samples dispersed in KBr pellets (1−2 wt %) were recorded with an IBM Model IR 40S spectrometer.

Thermogravimetric analyses (TGA) were carried out under N_2 for solid samples weighing ∼70 mg on a Cahn 121TG System at a heating rate of 5 °C/min.

Nitrogen adsorption/desorption isotherms at liquid nitrogen temperature were obtained on a Coulter Omnisorb (TM) 360CX sorptometer using ultrahigh purity nitrogen as the adsorbate and helium as the carrier gas. Samples of about 100 mg were outgassed overnight at 130 °C under a vacuum of 10^{-5} Torr. Surface areas (SBET) were obtained by the BET method.[18] For pillared and nonpillared LDH intercalates, the BET equation was applied over the partial pressure ranges of $0.05 < P/P_0 < 0.1$ and $0.05 < P/P_0 < 0.2$, respectively, where correlation coefficients were near one, in accord with previous surface area/pore analyses of pillared clays.[19] The *t*-plot method[20] was used to determine the total (S_t) and microporous (S_m) surface areas.

Transmission electron microscopy (TEM) was carried out with a JEOL 100 CX instrument at the Center for Electron Optics at MSU. Specimens for TEM imaging were prepared by dipping copper grids coated with holey carbon films into an aqueous suspension of the solid and allowing the water to evaporate. Energy dispersive spectroscopy (EDS) was performed using the same instrument in STEM mode (44 Å beam size) in order to obtain compositional information.

Elemental analyses were performed by ICP emission spectroscopy at the Toxicology Laboratory at MSU. About 15 mg of solid sample was dissolved in 50 mL of 1.5 vol % HNO_3 solution for each analysis.

Results and Discussion

As is summarized in Figure 2, at least six different approaches, designated methods I−VI, have been reported for the pillaring of layered double hydroxides by polyoxometalate anions with Keggin ion structures.[4−10] Among all of these approaches, method I represents the direct most efficient pathway as it affords the desired product by direct coprecipitation reaction of M^{2+}, M^{3+}, and POM^{n-}. However, this method has been shown to be useful only for acidic LDH derivatives, such as those with layer compositions of the type $[Zn_{1-x}Al_x(OH)_2{}^{x+}]$. Efforts to prepare pillared forms of typically basic LDH derivatives, e.g., layer compositions of the type $[Mg_{1-x}Al_x(OH)_2{}^{x+}]$, afford instead poorly ordered salts of the POM (see below) or base-hydrolyzed derivatives of the POM.

Method II involves an ion exchange reaction between a simple LDH−chloride or −nitrate and the pillaring POM. This was the method used to prepare the first examples of pillared LDH derivatives based on $V_{10}O_{28}^{6-}$ and $XM_{12}O_{40}^{n-}$ Keggin ions as the pillaring anion.[4,6] The key to successfully implementing ion exchange method II is to utilize a LDH−chloride or −nitrate precursor that has been prepared by coprecipitation, but which has not been isolated from suspension and dried. Drying the precursor even at ambient temperature removes water from the metastable hydrate formed in the coprecipitation reaction, and this renders the gallery surfaces less accessible for ion exchange. Consequently, the ion exchange reactions of desired LDH precursor with POM anions are difficult to complete, and prolonged exchange reactions typically are accompanied by hydrolysis reactions that afford undesirable byproducts. The importance of fully hydrated LDH precursors for pillaring ion exchange reactions has been emphasized recently by Clearfield and his co-workers.[9]

Methods III, IV, and V, which are the pathways of interest in the present work, all utilize a readily synthesized LDH−carbonate[21] as the starting material. Pathway III, as originally described by Chibwe and Jones,[7] converts the LDH−carbonate to a mixed-metal oxide solid solution,[17] which is then allowed to undergo a hydrolytic reconstitution reaction in the presence of the POM to form the LDH−POM. In contrast, pathways IV and V allow the mixed metal oxide to undergo reconstitution reaction in the absence of POM to form first a synthetic meixnerite intermediate, wherein the gallery anion is hydroxide. The LDH−hydroxide can then be allowed to react with an organic acid according to pathway IV to form an organo anion precursor,[8] which subsequently is converted by ion exchange reaction to the pillared LDH−polyoxometalate.[5,8] Alternatively, the LDH−hydroxide can be converted directly to the LDH−POM intercalate by direct ion exchange reaction.[22] This latter pathway is somewhat surprising, because POMs are readily hydrolyzed in basic solution.[23] However, the hydroxide ion is readily displaced from the gallery surfaces by POM^{n-}, and the immobilized POM^{n-} is stabilized toward basic hydrolysis.

The preparation of LDH−POM intercalates as represented by methods IV and VI in Figure 2 are chemically equivalent insofar as they both utilize an anion exchange reaction between an organo anion precursor and the pillaring POM^{n-}. This can be exceptionally efficient conversion as evidenced by the original work of Drezdzon.[5] However, method VI utilizes a coprecipitation reaction to prepare the organo anion precursor, whereas method IV makes use of the reaction of an organic acid with an LDH hydroxide. The latter acid−base reaction is less susceptible to competing side reactions (e.g., organoanion salt formation) than the coprecipitation reaction. Consequently, method IV generally is preferred over method VI. Also, we should note that the recently reported reaction of LDH−carbonate with glycerol at elevated temperatures (160−180 °C) most likely involve the formation of LDH glycerolates.[24] The glycerolates and related polyol derivatives show considerable promise as precursor to POM^{n-}-pillared products.[25]

We now consider the relative merits of pathways III, IV, and V, for the synthesis of LDH intercalates pillared by α-$H_2W_{12}O_{40}^{6-}$ Keggin ions. As shown by the XRD patterns in Figure 3, all three methods afford reaction products containing a 001 reflection corresponding to a pillared Mg_3Al−LDH phase with a basal spacing of ∼14.7 Å. In addition, each method produces a byproduct characterized by a broad reflection near $2\theta = \sim 8°$ (11 Å). The same byproduct also is observed for derivatives prepared by reaction pathways I, II, and VI. All efforts to

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(18) Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309.

(19) Butruille, J.-R.; Pinnavaia, T. J. In *Characterization of Catalytic Materials*; Butterworth-Heinemann: Boston, MA, 1992; p 149.

(20) De Boer, J. H.; Lippens, B. C.; Linsen, B. G.; Broekhoff, J. C. P.; Van den Heuvel, A.; Osinga, Th. J. *J. Colloid Interface Sci.* **1966**, *21*, 405.

(21) Cavani, F.; Trifirò, F.; Vaccari, A. *Catal. Today* **1991**, *11*, 173.

(22) Dimotakis, E. D.; Pinnavaia, T. J. Unpublished results.

(23) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: New York, 1983.

(24) Hansen, H. C. B.; Taylor, R. M. *Clay Miner.* **1991**, *26*, 311.

(25) Yun, S. K.; Pinnavaia, T. J. *Microporous Mater.* **1995**, *4*, 21.

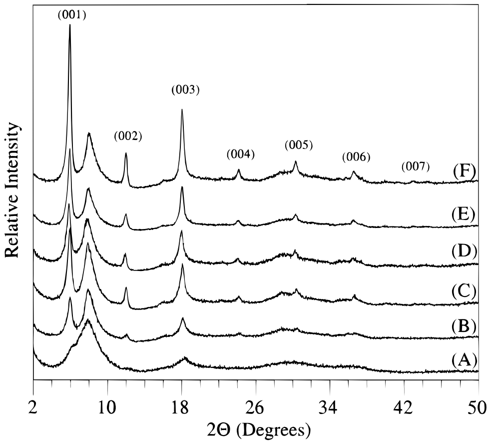
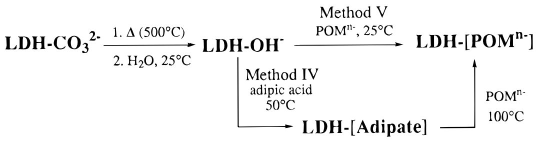


Figure 3. XRD patterns of $Mg_3Al-LDH-[\alpha\text{-}H_2W_{12}O_{40}{}^{6-}]$ reaction products prepared from the following: (A) a mixed metal oxide precursor by method III at 25 °C; a LDH−hydroxide (meixnerite) by method V at (B) pH 4.5, 25 °C, (C) ambient pH, 25 °C, 0.5 h, (D) ambient pH, 25 °C, 5 h, (E) at ambient pH, 70 °C, 5 h; and (F) a LDH−adipate by method IV at ambient pH, 70 °C, 5 h.

circumvent byproduct formation or to remove the byproduct by selective dissolution have been unsuccessful. The nature of the undesired byproduct will be discussed more fully below.

Returning to the XRD patterns in Figure 3, we see from part A that the reconstitution reaction of a mixed metal oxide in the presence of the Keggin ion according to method III affords a very poor yield of pillared product, the major product being the undesired 11 Å phase. The yield of pillared product obtained by ion exchange reaction of the LDH hydroxide with the Keggin ion (method V) is improved by conducting the reaction at ambient pH and at an elevated reaction temperature (cf., Figure 3, parts B−E). The best yield of the pillared phase, however, is provided by method V, which utilizes an LDH−adipate precursor for ion exchange reaction with the Keggin ion (cf., Figure 3, part F). The product obtained from this latter method exhibited 7 orders of (00l) reflection, corresponding to a basal spacing of 14.5 Å. As shown by the XRD patterns in Figure 4A, the byproduct formation can be further reduced by increasing the reaction temperature to 100 °C. Taking the layer thickness of the Mg_3Al−LDH as 4.8 Å, one obtains a gallery height of 9.7 Å, which is consistent with the van der Waals diameter (10.2 Å) estimated from crystallographic data for a Keggin ion salt.[26] The interlayer $\alpha\text{-}H_2W_{12}O_{40}{}^{6-}$ ion most likely has the C_2 axis of the oxygen framework orthogonal to the LDH layers to optimize H bonding to the gallery hydroxyl groups, as proposed previously.[6] Also, we note that the pillared $Mg_3Al-[\alpha\text{-}H_2W_{12}O_{40}{}^{6-}]$ intercalate was stable to 200 °C under N_2, as judged by the XRD patterns shown in Figure 4A.

On the basis of the above results for the pillaring of a Mg_3Al−LDH by $\alpha\text{-}H_2W_{12}O_{40}{}^{6-}$ Keggin ion, we investigated the effectiveness of methods IV and V for LDH pillaring by Dawson and Finke POM^{n-} ions. The reaction conditions utilized for the two methods are summarized in the following scheme:



The reaction temperature (25 vs 100 °C) and the use of a gallery expanding agent (adipate) were considered as potentially important factors in determining the gallery orientations of the cylindrical Dawson and Finke POM^{n-} ions.

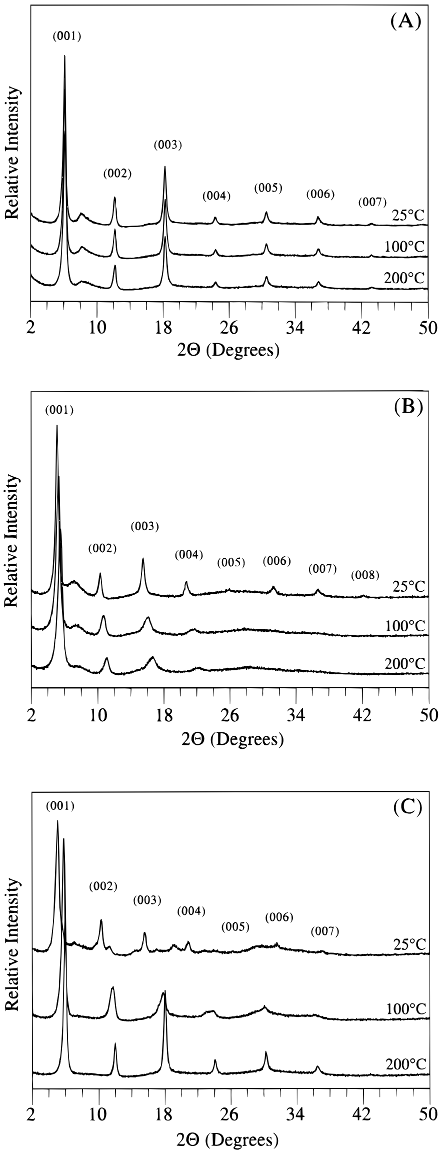


Figure 4. XRD patterns of the oriented films of (A) the $LDH-[\alpha\text{-}H_2W_{12}O_{40}{}^{6-}]$, (B) $-[\alpha\text{-}P_2W_{18}O_{62}{}^{6-}]$, and (C) $-[Co_4(H_2O)_2(PW_9O_{34})_2{}^{10-}]$ intercalates prepared by method IV using a Mg_3Al−adipate precursor. Diffraction patterns were taken at room temperature after drying under N_2 flow for 1 h at the temperature indicated.

The crystalline product obtained by the reaction of the Mg_3Al−adipate with the Dawson $\alpha\text{-}P_2W_{18}O_{62}{}^{6-}$ ion at 100 °C (method IV) exhibited 8 orders of (00l) reflection (Figure 4B). The basal spacing of 17.6 Å was in good accord with the sum of the estimated van der Waals diameter of the POM along the short (C_2) axis (12.3 Å)[27] and the LDH layer thickness (4.8 Å). The gallery $\alpha\text{-}P_2W_{18}O_{62}{}^{6-}$ anions, therefore, have the C_2 axis orthogonal to the LDH layers in order to optimize the H-bonding interactions between the LDH layer hydroxyls and the apical oxygen atoms on the POM oxygen framework. The $LDH-[\alpha\text{-}P_2W_{18}O_{62}{}^{6-}]$ intercalate also was thermally stable up to 200 °C under N_2. Small decreases in basal spacing due to dehydration are observed for the pillared product dried over the temperature range 25−200 °C.

In contrast to the product obtained from the LDH adipate precursor, the intercalate formed by the reaction of the Dawson

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[26] Spirlet, M.-R.; Busing, W. R. *Acta Crystallogr.* **1978**, *B34*, 907.

[27] D'Amour, V.-H. *Acta Crystallogr.* **1976**, *B32*, 729.

Table 1. Gallery Height (Å) of Pillared LDH−POM Intercalates Prepared from a LDH−OH⁻ Precursor at 25 °C and a LDH−Adipate Precursor at 100 °C

	α-$H_2W_{12}O_{40}^{6-}$ (10.2 Å × 10.2 Å)[a]		α-$P_2W_{18}O_{62}^{6-}$ (12.3 Å × 14.4 Å)[a]		$Co_4(H_2O)_2(PW_9O_{34})_2^{10-}$ (13.2 Å × 11.8 Å)[a]	
drying temp,[b] °C	LDH−OH⁻ 25 °C	LDH−adipate 100 °C	LDH−OH⁻ 25 °C	LDH−adipate 100 °C	LDH−OH⁻ 25 °C	LDH−adipate 100 °C
25	10.1	9.70	14.5	12.8	13.3	12.6
100	9.70	9.70	12.6	11.8	10.5	10.5
200	9.70	9.70	12.0	11.1	10.1	10.1

[a] Values in parentheses are the calculated van der Waals dimensions (Å) of each POM anion. [b] The LDH−POM intercalates were dried for 1 h under N_2 at the temperatures indicated.

ion with the meixnerite-like Mg_3Al−LDH hydroxide at room temperature (method V) gave a product with a basal spacing of 19.3 Å, implying that the long (C_3) axis of the α-$P_2W_{18}O_{62}^{6-}$ ion is orthogonal to the LDH layer stacking direction. The observed gallery height of 14.5 Å is consonant with the estimated van der Waals diameter of 14.4 Å for the POM along the C_3 axis,[27] assuming that there is no water molecule between the POM and the LDH layers. At a temperature of 100 °C the basal spacing decreased from 19.3 to 17.4 Å. This observation suggests that the gallery α-$P_2W_{18}O_{62}^{6-}$ ion reorients from an end-on position at room temperature to a horizontal position upon the thermal dehydration of the gallery water. With the C_3 axis of the α-$P_2W_{18}O_{62}^{6-}$ oxygen framework orthogonal to the LDH layers, six apical oxygen atoms may participate in H-bonding with the LDH hydroxyl groups, whereas 14 terminal oxygen atoms become available for H-bonding with the C_2 axis orthogonal. It was not possible to return to the POM to an end-on orientation by rehydration with water. Thus, the room temperature product with a 19.3 Å spacing is metastable.

The air-dried LDH derivative pillared by Finke-type $Co_4(H_2O)_2(PW_9O_{34})_2^{10-}$ ions at 100 °C using the Mg_3Al−LDH−adipate as a precursor (method IV) exhibited a basal spacing of 17.4 Å. This intercalate was thermally stable up to 200 °C under N_2 (Figure 4C). The air-dried product formed from the LDH−hydroxide by reaction with the same POM at 25 °C (method V) showed a basal spacing of 18.1 Å. On the basis of the estimated size of this Finke type POM,[15] both intercalated products have the C_2 axis of the POM orthogonal to the LDH layers. Once heated, the gallery POM comes in closer contact with the LDH layers to optimize favorable H-bonding interactions, which is the case for the POM orientation in the pillared product prepared by method IV.

Table 1 summarizes the gallery heights for the LDH−POM intercalates at different drying temperatures. Each intercalate showed different gallery contractions upon thermal treatment. Air-dried LDH−POM intercalates exhibited gallery heights in very good agreement with the expected values based on the proposed gallery POM orientations. Upon heating, all the intercalates showed a decreased gallery height. Removal of interlayer water occurs upon heating, resulting in stronger electrostatic and H-bonding interactions between POMs and LDH layer hydroxyl groups. This will cause the POM to adopt a thermodynamically stable gallery orientation. Pillar reorientation at ≥100 °C, therefore, appears to be responsible for the observed gallery contractions of 2.5 Å and 3.2 Å for the LDH−[α-$P_2W_{18}O_{62}^{6-}$] and −[$Co_4(H_2O)_2(PW_9O_{34})_2^{10-}$] products, respectively, prepared by method V. At 200 °C the α-$H_2W_{12}O_{40}^{6-}$ intercalated LDH showed only a 0.2−0.4 Å decrease in the gallery height, whereas the LDH−[α-$P_2W_{18}O_{62}^{6-}$] and −[$Co_4(H_2O)_2(PW_9O_{34})_2^{10-}$] products prepared by method IV showed 1.7 and 2.5 Å decreases, respectively. The pillared products obtained by methods IV and V showed essentially the same gallery height at 200 °C, indicating the same gallery orientation of the POM pillars at this stage. Figure 5 illustrates the observed gallery orientation of the three POM pillars in the products obtained after drying (≥100 °C).

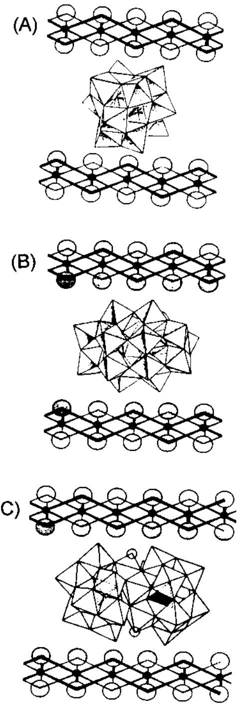

Figure 5. Proposed POM^{n-} gallery orientations for the LDH intercalates after drying (≥100 °C) under N_2: (A) α-$H_2W_{12}O_{40}^{6-}$, (B) α-$P_2W_{18}O_{62}^{6-}$, and (C) $Co_4(H_2O)_2(PW_9O_{34})_2^{10-}$. The open circles of the LDH phase represent the hydroxyl groups and the filled circles are the metal ions in octahedral sites.

On the basis of the observed gallery heights of the LDH−POM intercalates dried at 100−200 °C, we propose that the POMs are strongly bound to the LDH layers by electrostatic and hydrogen bonding forces, because the observed gallery heights are somewhat smaller than the minimum van der Waals dimension of the POM. Hydrogen bonding interactions, therefore, seem to be an important factor for determining the gallery orientation of the POM. Charge matching between the POM and the LDH layers controls the lateral separation of POM pillars in the gallery space.

The retention of the Dawson α-$P_2W_{18}O_{62}^{6-}$ structure in the intercalated state was verified by the FTIR spectra shown in Figure 6. The stretching frequencies for the P−O linkages at 1092 and 1020 cm^{-1} and for the W−O bonds at 957, 912, and 756 cm^{-1} are very similar for the authentic potassium salt of the POM[14] and the LDH intercalate prepared by method IV. However, the product prepared by method V showed ν(W−O) modes slightly shifted by 3−8 cm^{-1} to lower frequency, probably due to a different POM orientation and a local change in the chemical environment around the oxygen framework. The two Finke-ion pillared products prepared by methods IV and V showed basically the same vibrational modes of the oxygen

Table 2. Chemical Compositions and Surface Areas of $Mg_{1-x}Al_x$−LDH Intercalates[a]

A^{n-}	precursor	composition (Mg:Al:W)	S_{BET}, m^2/g	S_t, m^2/g	S_m, m^2/g	% S_m
CO_3^{2-}	direct precipitation	3.11:1.00:0	104	112	0	0
OH^-	LDH−CO_3^{2-}	3.08:1.00:0				
α-$H_2W_{12}O_{40}^{6-}$	LDH−adipate (100 °C)	2.23:1.00:1.96	120	136	70	51
α-$P_2W_{18}O_{62}^{6-}$	LDH−adipate (100 °C)	1.88:1.00:3.06	99	100	29	29
$Co_4(H_2O)_2(PW_9O_{34})_2^{10-}$	LDH−adipate (100 °C)	2.46:1.00:1.94	112	108	42	39

[a] S_{BET} is the Brunauer−Emmett−Teller surface area; S_t and S_m are the total and microporous surface areas, respectively, obtained by the *t*-plot method.

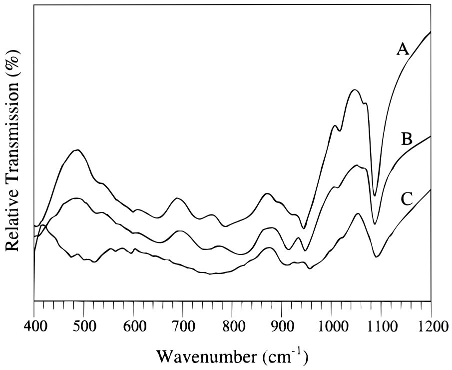

Figure 6. FTIR spectra of LDH−[α-$P_2W_{18}O_{62}^{6-}$] intercalates: (A) prepared at 100 °C from a Mg_3Al−LDH−adipate precursor and dried at 25 °C; (B) prepared at 25 °C from a Mg_3Al−LDH−OH^- precursor and dried at 25 °C. Spectrum C is for the authentic salt K_6[α-$P_2W_{18}O_{62}^{6-}$].

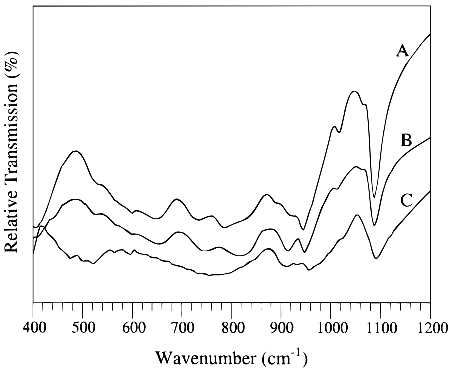

Figure 7. FTIR spectra of LDH−[$Co_4(H_2O)_2(PW_9O_{34})_2^{10-}$] intercalates: (A) prepared at 100 °C from a Mg_3Al−LDH−adipate precursor and dried at 25 °C; (B) prepared at 25 °C from a Mg_3Al−LDH−OH^- precursor and dried at 25 °C. Spectrum C is for the authentic salt $K_{10}[Co_4(H_2O)_2(PW_9O_{34})_2^{10-}]$.

framework of the gallery α-$P_2W_{18}O_{62}^{6-}$, as shown in Figure 7. The stretching vibrations characteristic of P−O (1038 cm^{-1}), terminal W−O (961 and 941 cm^{-1}), corner-sharing W−O−W (884 $cm^{-1)}$, and edge-sharing W−O−W (772 and 739 cm^{-1}) linkages in $K_{10}[Co_4(H_2O)_2(PW_9O_{34})_2^{10-}]$[14,28] were observed at very similar positions for the LDH intercalates prepared by both synthesis methods.

TEM images of the original LDH−carbonate and the POM intercalates were consistent with the topochemical nature of the pillaring reactions. Hexagonal crystals ranging from 600 to 2500 Å in diameter were observed for the intercalates before and after the pillaring reactions. However, important compositional changes accompany the pillaring reactions.

Table 2 summarizes the elemental analyses and the textural properties of the original Mg_3Al−LDH−carbonate used to prepare the meixnerite precursor and the LDH−POM intercalates obtained at 100 °C from the adipate precursor (method IV). As has been observed previously for LDH pillaring reactions with vanadate[9] and Keggin ions,[11] some of the layer Mg^{2+} ions were depleted upon pillaring. In our studies a basic suspension of the meixnerite (pH ∼11.3) was introduced either directly to the POM solution (method V) or to the adipic acid (method IV). The reaction pH measured at room temperature after reaction with the POMs was in the range of 7.0−8.0 in absence of adipate and about 6.5 in the presence of adipic acid. A decrease in the reaction pH upon pillaring is indicative of the depletion of the more basic Mg^{2+} ions, as was previously observed in a study of the physicochemical properties of Mg_{1-x}-Al_x−LDHs.[17]

The products obtained from the LDH−adipate precursor (method IV) showed more Mg^{2+} depletion than the product obtained using meixnerite (method V). For example, the starting Mg_3Al−LDH−carbonate gave a Mg^{2+} to Al^{3+} ratio of 3.11, but the LDH−[α-$H_2W_{12}O_{40}^{6-}$] product derived from LDH−adipate showed a Mg^{2+} to Al^{3+} ratio of 2.23, and the product derived from meixnerite gave 2.84. Also, the Dawson and Finke POM^{n-}-pillared derivatives prepared from meixnerite at 25 °C exhibited Mg^{2+}/Al^{3+} ratios of 2.82 and 3.07, respectively. But, the Mg^{2+}/Al^{3+} ratios for the LDH intercalates prepared at 100 °C from the LDH−adipate were 1.88 and 2.46, respectively. On the basis of changes in chemical composition, therefore, the high temperature pillaring reactions are not topotactic.

As shown by the surface area data in Table 2 for the POM pillared products prepared by method IV, the textural properties of the initial Mg_3AlCO_3−LDH were greatly changed upon pillaring reactions with POMs. All LDH−POM intercalates exhibited type I N_2 adsorption isotherms at lower P/P_0 values, and H1 type hysteresis loops at higher P/P_0, indicating the presence of both intragallery micropores and interparticle mesopores, respectively. About 30−50% of the surface areas of LDH−POM intercalates arises from gallery micropores, whereas no microporous surface area was observed for the starting Mg_3Al−LDH−carbonate. Increasing the size of the POM pillar from α-$H_2W_{12}O_{40}^{6-}$ to α-$P_2W_{18}O_{62}^{6-}$ resulted in decreased microporous surface area from 69.5 to 28.5 m^2/g. The larger size of the Dawson ion is expected to a afford smaller gallery space than the Keggin POM. As expected from the size, charge, and gallery orientation of the Finke ion, the LDH−[$Co_4(H_2O)_2(PW_9O_{34})_2^{10-}$] intercalate exhibited a larger microporous surface area (42.0 m^2/g) compared to the Dawson POM-pillared derivative, but smaller than Keggin ion intercalate.

Since the equivalent weights of our pillared LDH derivatives are much larger than other porous materials and vary markedly depending on the POM, we propose a comparison of surface areas based on a unit of layer charge (e^+). As is shown in Table 3, the surface area per equivalent weight of LDH can be

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(28) Rocchiccioli-Deltcheff, C.; Thouvenot, R.; Franck, R. *Spectrochim. Acta, Part A* **1976**, *32A*, 587.

(29) Behrens, P. *Adv. Mater.* **1993**, *5*, 127.

(30) Yamanaka, S.; Hattori, M. In *Chemistry of Microporous Crystals*; Elsevier: Amsterdam, 1991; Vol. 60, p 89 and references therein.

(31) (a) Bottero, J. Y.; Cases, J. M.; Fiessinger, F.; Poirier, J. E. *J. Phys. Chem.* **1980**, *84*, 2933. (b) Brindley, G. W.; Yamanaka, S. *Am. Mineral.* **1979**, *64*, 830.

Table 3. Surface Areas of POM-Pillared LDH Intercalates[a]

LDH−[A^{n-}]	S_{BET}, $Å^2/e^+$	S_t, $Å^2/e^+$	S_m, $Å^2/e^+$	% S_m
$[Mg_{3.11}Al_1(OH)_{8.22}]-[CO_3^{2-}]_{0.50}$ (fw 272.37)	4.69	5.05	0	0
$[Mg_{2.23}Al_1(OH)_{6.46}]-[\alpha\text{-}H_2W_{12}O_{40}^{6-}]_{0.17}$ (fw 675.24)	13.5	15.2	7.79	51
$[Mg_{1.88}Al_1(OH)_{5.76}]-[\alpha\text{-}P_2W_{18}O_{62}^{6-}]_{0.17}$ (fw 912.38)	15.0	15.2	4.32	29
$[Mg_{2.46}Al_1(OH)_{6.92}]-[Co_4(H_2O)_2(PW_9O_{34})_2^{10-}]_{0.10}$ (fw 677.55)	12.6	12.2	4.73	39

[a] S_{BET} is the Brunauer−Emett−Teller surface; S_t and S_m are the total and microporous surface areas, respectively, obtained by the *t*-plot method. All surface areas are reported in units of $Å^2$ per LDH unit charge.

expressed in $Å^2/e^+$ units. This unit provides a more structurally relevant indication of the textural properties of the LDH−POM intercalates than the conventional m^2/g unit. BET/N2 surface areas were increased from 4.69 $Å^2/e^+$ for Mg_3AlCO_3 to 15.0 $Å^2/e^+$ for the POM pillared derivative. Microporous surface areas of 4.32−7.79 $Å^2/e^+$ were accessible by N_2 molecule for the pillared LDH−POM derivatives.

An interesting feature observed in the XRD of all LDH−POM intercalates was the broad X-ray reflections centered at ∼11 Å (Figures 3 and 4) attributed to an impurity byproduct, as was mentioned earlier. For the intercalates with the same POM, the 2θ position of this phase was found at nearly the same position independent of the LDH−POM product. However, for LDHs interlayered with different POMs, the impurity reflections occurred at a somewhat different positions of 2θ. Interestingly, upon heating, this reflection showed not only a reduced intensity but also a shift toward higher 2θ (Figure 4). Both the intensity and position of the reflection were recovered upon rehydration. Considering the potential importance of pillared LDH−POM compounds for materials applications, a more precise assignmemt of the impurity phase is desired.

There are five possible structural models, including three suggested earlier,[9,10,12] for the observed impurity byproduct, each of which may account for the broad XRD reflections. They are as follows: (i) a pillared derivative formed by intragallery hydrolysis of the initial POM; (ii) a pillared LDH derivative containing the same POM as the principal product, but with a different gallery orientation; (iii) a pillared derivative with the POMs grafted to the LDH layers by displacement of the layer OH groups by oxygen atoms of the POM, ass suggested by Clearfield and co-workers;[9] (iv) a partially intercalated LDH−POM phase with the majority of the interlayer species being occupied by smaller anions such as Cl^- or CO_3^{2-}, as suggested by Weber, et al.;[12] (v) a salt formed from cations depleted from the layered structure (e.g., Mg^{2+}) and nongallery POM during the pillaring reaction, as suggested by Pinnavaia and co-workers.[10]

Since the molecular configuration of a Keggin type POM is almost spherical with a diameter near 10 Å, the *d* spacing (∼11 Å) of the impurity phase in these systems can not be due to a pillared phase with a different POM orientations in the gallery. In addition, the FTIR spectra for an authentic POM and the LDH−POM intercalates clearly showed the absence of hydrolyzed POM species at a concentration commensurate with the impurity phase. Thus, possibilities i and ii are precluded by these results. Possibility iii, involving a grafted LDH−POM species formed by displacement of the layer OH groups by POM oxygen atoms, is consistent with the observed d spacing for the impurity, at least when the POM is a Keggin ion. But, the appearance of an impurity phase is not POM ion specific, as might be expected for a grafted structure requiring a commensurate relationship between the POM and the triangular hydroxyls being replaced in the LDH layer. Also, the unique thermal behavior of the impurity phase, that is, its change in position and intensity upon heating and rehydration, can not be explained by this proposal. Model iv for the impurity phase, which is based on mixed ion intercalation, is precluded by chemical analysis (see Table 2) and by the absence of carbonate or nitrate vibrations in the FTIR spectra.

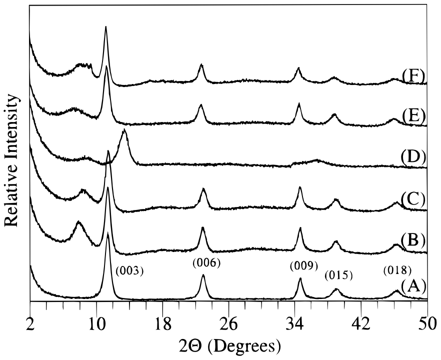

Figure 8. Powder XRD patterns showing impurity phase reflections, as well as (00l) reflections for POM-pillared LDHs: (A) Mg_3AlCO_3; (B) solid product obtained by allowing solid Mg_3AlCO_3 to react with a 3-fold excess of aqueous $\alpha\text{-}H_2W_{12}O_{40}^{6-}$ at room temperature for 1 h. The XRD of sample B was then recorded after heating at (C) 100 °C and (D) 200 °C for 1 h under N_2. (E) XRD pattern of sample D after rehydration in water for 30 h. (F) XRD pattern of the product obtained by the solid state reaction of Mg_3AlCO_3 and $\alpha\text{-}H_2W_{12}O_{40}^{6-}$.

Salt formation, model v, remains the favored explanation for the impurity phase. As shown earlier, the metal ions, particularly Mg^{2+}, can be extracted from the LDH layers upon pillaring. Depending on pH, these metal ions can form hydrolyzed species of $[M_a^{x+}(OH)_b(H_2O)_c]^{(ax-b)}$ in aqueous media, which can then form an ionic salt as a byproduct upon reaction with POM molecules during the pillaring reaction. A systematic experimental approach to the identity of the impurity phase has been attempted in the present work. We found that the simple addition of a POM solution to an aqueous suspension of Mg_3AlCO_3−LDH under the same reaction conditions used in the pillaring reaction resulted in products that contained the same broad XRD reflections as observed for the impurity phase contained in all $Mg_3Al-[\alpha\text{-}H_2W_{12}O_{40}^{6-})]$ intercalates (Figure 8A,B). The room temperature reaction of a Mg_3AlCO_3 suspension in the POM solution does not undergo ion exchange to yield a LDH−POM intercalate due to the high preference for interlayer carbonate anions.[32] Therefore, it is clear that XRD reflections of the reaction product is not due to a pillared phase but to a new phase formed by a structural modification of the LDH.

The product formed from the Mg_3Al−LDH−carbonate and $\alpha\text{-}H_2W_{12}O_{40}^{6-}$ exhibited the same thermal behavior as the impurity phase formed in the synthesis of $Mg_3Al-[\alpha\text{-}H_2W_{12}O_{40}^{6-}]$ intercalates. Thermal treatment was found to cause the impurity reflections to move toward higher 2θ with an accompanying decrease in intensity (cf., Figure 8C,D). Upon rehydration the reflection returned to the original position as found in the unheated initial sample (Figure 8E). The XRD properties of the product formed from Mg_3Al−LDH−carbonate

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(32) (a) Reichle, W. T. *Chemtech* **1986**, 58. (b) Carrado, K. A.; Kostapapas, A.; Suib, S. L. *Solid State Ionics* **1988**, *26*, 77.

and α-$H_2W_{12}O_{40}{}^{6-}$ are analogous to the poorly ordered M^{2+}–POM salts formed by coprecipitation[10] or by replacement of a monovalent cations in a well crystallized POM with di- or trivalent countercation.[33,34]

Even the solid state reaction of a Mg_3Al–LDH–carbonate (2.26×10^{-4} mol) and a well-crystallized POM salt (3.12 to 6.23×10^{-6} mol), caused by grinding the solids with a mortar and pestle, showed the same byproduct XRD reflections (Figure 8F). Also, the product formed by the solid state reaction of a well order monvalent cation salt of a POM and $Mg(OH)_2$, where no intercalation whatsoever is expected, exhibited the same impurity reflections. This observation provides key evidence that the impurity byproduct is not a intercalated phase but rather a poorly ordered ionic salt of the POM formed on the external surface of the LDH layers.

The XRD reflections of all the impurity byproducts formed in the synthesis of the LDH–[α-$H_2W_{12}O_{40}{}^{6-}$)], –[α-$P_2W_{18}O_{62}{}^{6-}$], and –[$Co_4(H_2O)_2(PW_9O_{34})_2{}^{10-}$)] intercalates also were observed at the same 2θ positions as the products obtained by reaction of Mg_3AlCO_3 with the corresponding POM in aqueous suspension or in solid state. As expected, the products obtained by the aqueous reaction of the POM and the Mg_3AlCO_3 did not exhibit any microporous surface area. This latter result also indicates that the impurity byproduct is not a pillared LDH containing grafted POM ions.

Energy dispersive X-ray spectroscopic analysis of the solid product obtained by the reaction of Mg_3AlCO_3 and POM in H_2O provided additional evidence supporting our assignment of the impurity byproduct phase. The product retained the morphology of the initial LDH–carbonate, namely, hexagonal crystals approximately 2000 Å in diameter. Spot mode scanning with a beam diameter of 44 Å showed almost constant Mg/Al and W/Al ratios of 3.60 and 1.03, respectively, at the center of the crystal. However, the edges of the crystals showed a lowered Mg/Al and W/Al ratio of 2.21 and 0.99, respectively. Between the center and edge locations, we observed Mg/Al and W/Al ratios of 3.52 and 1.37, respectively. The EDS results, together with the XRD results, clearly demonstrate that the impurity byproduct is a magnesium rich salt deposited on the basal planes of the LDH crystal. The salt most likely forms by migration of Mg^{2+} (and some Al^{3+} ions) from edge sites to sites on the basal surfaces.

The POM salt impurity on the external surfaces of the LDH host is highly disordered. Depending on the POM, the main reflection occurs near 11.0 Å, and two weaker reflections are observed at ∼5.2 and ∼3.1 Å, consistent with higher order 00l reflections of a lamellar structure. Attempts to dissolve the salt impurity from the surface of the host by washing with dilute acid (0.1 M HNO_3) or base (0.1 M NaOH) resulted instead in the destruction of the layered structure of LDH–POM intercalate.

Conclusions

Pillared derivatives of Mg_3Al layered double hydroxides (LDH) with polyoxometalate (POM) anions of Keggin (α-$H_2W_{12}O_{40}{}^{6-}$), Dawson (α-$P_2W_{18}O_{62}{}^{6-}$), and Finke ($Co_4(H_2O)_2(PW_9O_{34})_2{}^{10-}$) structures were obtained by ion exchange methods. The reaction of a Mg_3Al–LDH–adipate, formed by the reaction of meixnerite with adipic acid, with the desired POMs at 100 °C afforded products that were more highly crystalline than those obtained by reaction with the LDH hydroxide (meixnerite) or by other pillaring methods (see Figure 2). Pillaring reactions of Mg_3Al–LDH adipate precursor resulted in the depletion of some Mg^{2+} from the host LDH layers, but the hexagonal morphology of the crystal was retained after reaction. Different gallery heights for the same pillaring POM ion were observed for the Keggin (10.1 and 9.70 Å), Dawson (14.5 and 12.8 Å), and Finke (13.3 and 12.6 Å) POMs, depending on the reaction conditions employed. Pillaring reactions afforded access to the interlayer surfaces with up to 51% of the total surface area being due to micropores. The layered structures of the LDH–POM intercalates were thermally stable under N_2 up to 200 °C with retention of gallery micropores. The gallery orientation of the POM pillars was determined mainly by hydrogen-bonding interactions between the layer hydroxyl groups and oxygen framework of the POM anion. Changing the reaction temperature resulted in an important effect on the gallery orientation of the Dawson POM. In addition to intercalating into the galleries of the LDH host, the POM anions reacted with Mg^{2+} and Al^{3+} cations at the edges of the layers to form saltlike impurities on the external surface of the LDH crystals.

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(33) McGarvey, G. B.; Taylor, N. J.; Moffat, J. B. *J. Mol. Catal.* **1993**, *80*, 59.

(34) Brückman, K.; Tatibouët, J.-M.; Che, M.; Serwicka, E.; Haber, J. *J. Catal.* **1993**, *139*, 455.